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Effect of molar mass on enthalpy relaxation and crystal nucleation of poly (L-lactic acid)

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ABSTRACT

The effect of the chain length/molar mass of poly (L-lactic acid) (PLLA) on the formation of homogeneous crystal nuclei below and above the glass transition temperature (T_g) has been analyzed by fast scanning chip calorimetry, employing Tammann's nuclei development method. It has been found that the kinetics of crystal nucleation below T_g is independent on the chain length within the investigated range of molar masses from about 60 to 600 kDa, similar as the kinetics of enthalpy relaxation. In contrast, at temperatures well above T_g there is detected that crystal nucleation is slower in samples of higher molar mass. This observation is confirmed by non-isothermal nucleation experiments which showed that suppression of nucleation occurs on cooling at rates of 200, 100, and 30 K/s in samples with molar masses of around 60, 100, and 600 kDa, respectively. The different effect of molar mass on crystal nucleation in the glass and well above T_g is discussed in terms of the length-scale of required chain-mobility and of the critical size of nuclei.

1. Introduction

Poly (L-lactic acid) (PLLA) is a linear aliphatic polyester which is based on short-term renewable resources, with the potential to replace classical petroleum-based polymeric materials in all areas of application and justifying therefore ongoing intense research regarding all stages of the production-chain from the monomer to the final material. Similar as in all polymers, processing, structure and material properties of PLLA are largely controlled by the molecular architecture. Parameters include the concentration of minor amount of D-isomer co-units and the molar mass which both affect, among others, the crystallization behavior. Since the presence of crystals in PLLA controls important properties like the thermo-mechanical stability or the degradation rate, analysis of the relation between the chain structure and crystallization behavior is a superior task [1–3].

The effect of presence of small amount of D-isomer co-units in the chain and of the molar mass on melt-crystallization has extensively been investigated in the past. It was shown that the presence of D-isomer co-units in L-isomer rich chains leads to a decrease of the maximum achievable crystallinity such that samples with a D-isomer content higher than about 10% are fully amorphous or exhibit only negligible crystallinity. There was observed that the crystallization-temperature range and maximum crystallization rate decrease drastically even on addition of only low amount of D-isomer co-units. Similarly the maximum crystallization rate decreases with increasing the molar mass [4–11]. In addition, the effect of the chain structure on the specific α'/α -crystal polymorphism, evident on crystallization of the relaxed melt, was investigated [12,13].

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